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Lowest excited electron states in a large atomic cluster

M. Apostol
Department of Theoretical Physics,
Institute of Atomic Physics,
Magurele-Bucharestr MG-6,
POBox MG-35, Romania
email:apoma@theory.nipne.ro

Abstract

A rough estimate is given of the lowest energy electron states of a large atomic cluster.

Large atomic clusters of N atoms, with nuclear charges z_i, $i = 1, 2, ...N$, admit a quasi-classical description, especially for a metallic binding; electrons are distributed over single-particle states determined by the self-consistent potential energy $\sum \varphi_i$, where φ_i is the screened Coulomb field $\varphi_i = -e^2 z_i \exp(-q_i |\mathbf{r} - \mathbf{r}_i|) / |\mathbf{r} - \mathbf{r}_i|$; q_i is a self-consistency parameter, which may approximately be taken as the one corresponding to an isolated atom in the Thomas-Fermi model, $q_i = \alpha z_i^{1/3}$; where α is a numerical coefficient, e.g. $\alpha = 0.77 a_H^{-1}$, a_H denoting the Bohr radius; for conveniency, we may adopt the atomic units. In addition, for large atomic clusters one may neglect the shell effects for the electron states lying high in energy. The electron states are approximate plane waves $\psi_i = (1/\sqrt{v_i}) \exp(i\mathbf{k}(\mathbf{r} - \mathbf{r}_i))$ normalized over a volume v_i around a the i-th atom; actually they are so over intermediate distances, not very close to, not very far from the nuclei. The cluster orbital ("a quasi-classical molecular orbital $QCMO$") $\sum_i c_i \psi_i$ may serve for determining the splitting up of the atomic orbital ψ_i into an energy band, following the standard Bloch' or Huckel's techniques; to the nearest-neighbours (or tight-binding) approximation the typical off-diagonal matrix element reads

$$\frac{1}{v_i} \sum_{\langle ij \rangle} \int d\mathbf{r} \cdot \varphi_i(r) \cdot e^{i\mathbf{k}\mathbf{a}_{ij}} \quad , \tag{1}$$

where $\mathbf{a}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ are the nearest-neighbouring positions; one may employ an average over z_i and $\mathbf{a}_{ij}$, so that the integral is $\sim 0.6 z^{4/3}$; here, the volume v_i is that of a sphere of radius $R \sim 1/q$, according to the Thomas-Fermi estimations; the atomic orbital of energy $\varepsilon = \overline{\varepsilon}_i$ splits up into a band $\varepsilon(k) = \varepsilon - 1.2 z^{4/3} \sin ak$, where ak runs from $-\pi/2$ to $\pi/2$ (as a consequence of the average over a sphere); the average inter-atoms separation $a \sim R_c / N^{1/3}$, where R_c is the cluster radius; it may approximately be taken as $a \sim 1$, i.e. of the order of the Bohr radius. In the quasi-classical description of the cluster the energy levels are filled up to zero energy, as for a neutral cluster, i.e. the chemical potential is vanishing; therefore one may take $\varepsilon = 0$ in the above formula, and look at the half-band of negative energies

$$\varepsilon(k) = -1.2 z^{4/3} \sin ak \ , \ \ 0 < ak < \pi/2 \tag{2}$$

as the lowest electron states of the cluster arising from the zero-energy atomic orbital; they are separated by an amount of the order of $\sim z^{4/3}/N^{1/3}$; however, each of the rest of the atomic

orbitals is splited up too in the same manner; so that one may write the lowest energy electron states of the cluster as

$$\varepsilon_n \simeq -z^{1/3} \cdot n/N^{1/3} \quad , \quad n = 0, 1, 2, ...; \tag{3}$$

the result is valid for $1 \ll z \ll N$; an estimate of the chemical potential is $\varphi_0 \sim -z^{4/3}$. For a more metallic bond where the tight-binding approximation breaks up, the levels may ever be denser, as regards their dependence on n.

The high energy excited states of an atom are given by the Bohr-Sommerfeld quantization rules

$$\int p_r dr = \int \left[2 \left(-|E| - l(l+1)/2r^2 + \varphi \right) \right]^{1/2} dr = 2\pi\hbar(n_r + \gamma) \tag{4}$$

with standard notations; where n_r is the (large) radial quantum number and $\gamma = 1/2$ is a quantal correction; the potential $\varphi = ze^{-qr}/r$, while at large distances $\varphi = 1/r$, as for a cation; and for large l the quasi-classical $(l + 1/2)^2$ is more appropriate than $l(l+1)$; the integral is taken twice between the zeros of the radial momentum, *i.e.* along a complete classical orbit; one can see easily that the large r where p_r vanishes goes like $1/|E|$, and the centrifugal potential may be neglected to the first approximation; so that, a suitable scale change of r leads to $|E|^{1/2} \cdot (1/|E|) \sim n_r$; hence, $|E| \sim 1/n_r^2$, *i. e.* the atomic Rydberg's levels.